CHAPTER 1

INTRODUCTION

1.1 MEMBRANES

Chemical processes, in general, can be regarded as a sequence of a pretreatment step, a reaction step and a separation step, transforming the incoming raw materials (input) into the desired products (output). This transformation requires energy. Besides the desired product, often undesired by- or waste-products will also be produced. Engineering of chemical processes is more and more carried out in the framework of the minimization of energy consumption and waste disposal. To fulfill the tasks of diminishing energy consumption and minimization of waste, modular, energy efficient and highly selective separation techniques are required.

During the last three decades, the membrane processing technique has emerged as a separation process which is competitive in many ways with conventional separation techniques, such as distillation, fractionation, adsorption, absorption, extraction etc. The conventional methods of separation, from environmental and efficiency points of view, do not satisfy the increasing needs of most of the industries. Membrane separation technology, in its modern incarnation, is energy efficient and highly adaptive for a wide range of applications stemming from the development of new polymers or modifications of the existing polymers as membrane material. Pressure driven membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis have successfully been implemented in several industrial applications.
The membrane is a thin film. Both organic and inorganic polymer materials can be shaped into a wide variety of forms. The essential characteristics of a good membrane are with macromolecular morphology, good physical properties with a wide range of chemical properties, and a fair degree of physical and chemical stabilities. Several types of membrane separation mechanisms such as adsorption exist. In membrane applications where the sorption-diffusion mechanism plays the major role, the choice of the membrane material is based on selective sorption and diffusion properties.

Biological membranes are composed primarily of lipids and proteins (Jain 1980; Wagner 1980) e.g. skin, lings, heart-collagen, liver-collagen and kidney-glomerular membrane etc. Scientists have succeeded in developing synthetic membranes with the desired properties such as resistance towards temperature, pressure, solvent and microbial, with improved mechanical strength and pH stability (Michaels 1976). However, no synthetic membrane has yet been developed that can perform like living membranes. Efforts are being made continuously to develop membranes similar to that of natural biological ones.

Polyvinyl alcohol (PVA) blends have long been used with other natural polymers because of PVA’s ability to form films (Pal et al 2006). The performance properties of PVA are influenced by the molecular weight and the degree of hydrolysis. Gelatin is obtained by the thermal denaturation of collagen from animal skin, bones and rarely fish scales. It contains mainly the residues of 3 amino acids glycine (arranged every third residue), proline, and 4-hydroxyproline in its structure. Gelatin contains extended left-handed proline helix conformations incorporated with 300 to 4000 amino acids. The gelling properties of the gelatin can be altered by the introduction of chemical cross-links by using transglutaminase to link lysine to glutamine residues or glutaraldehyde to link lysine to lysine.
The biomaterial, gelatin and PVA are found to be mixed in each other and form a homogenous compatible material with cellulose acetate and also possess a film-forming property. Accordingly, it is used for making hard and soft gelatin capsules. Considering these compatibility and film-forming property, a PVA-gelatin with cellulose acetate film was thought to be a good candidate for making ultrafiltration membranes. Hence, attempts were made to develop an ultrafiltration membrane by esterifying the hydroxyl group of PVA with the carboxyl group of gelatin and mixed with cellulose acetate.

1.2 MEMBRANE SEPARATION PROCESS

In a membrane process, a membrane acts as a selective interphase between two bulk phases. By means of a driving force, some of the species from a multi-component mixture are transported through the membrane into the other bulk phase while other components are retained by the membrane. Selective mass transport has occurred. Often, a sufficiently high selectivity is accompanied by low transmembrane fluxes and vice versa, making a highly selective membrane process too expensive. A general illustration of all types of membrane separation processes is provided Figure 1.1.
Figure 1.1 Filtration spectrum
Future financial rejudgement of charges for waste disposal may favour highly selective separation processes like membrane processes which minimize waste streams and even offer a possibility to recycle valuable species from the effluent streams. Besides applications in chemical engineering, membranes are often used in medical applications. In fact, membrane sales are having the largest turnover in the artificial kidney business.

Because of the future prospective, especially in environmental engineering, membrane technology attracts a considerable amount of research interest. The research carried out in membrane technology can be roughly divided into two groups. The first group, the membrane process group, uses membranes with certain specified characteristics as a black box and studies its behaviour under certain process conditions as a singular process or, more often, as a hybrid process in combination with other unit operations. The other group is interested in material science aspects of membranes, e.g., the morphology of membranes, and how this morphology relates to the mass transport characteristics. Depending on the morphology, the applications for a given membrane can be very different.

The key component in all membrane separation processes is the membrane. A membrane can be described as a thin barrier between two bulk phases that permits transport of some components in a direction retaining others. A driving force is necessary to allow mass transport across the membrane. A schematic representation of the membrane process is given in Figure 1.2.

A review of the historical developments in membrane science and technology in general has been given by (Lonsdale 1982; Maso 1991). Reviews on the ultrafiltration process in particular have been presented by (Cheryan 1986; Michaels 1980).
Figure 1.2 Schematic representation of the membrane separation process

1.3 LITERATURE REVIEW

Many polymer components have been used for ultrafiltration (UF) membrane material such as cellulose acetate (CA), poly-acrylonitrile (PAN), polyethersulfone (PES), polysulfone (PS) and polyamide (Chen et al 2009; Rahimpour and Madaeni 2007; Bowen et al 2001; Hosch and Staude 1996). In case of UF membranes, the polymer material should exhibit excellent biocompatibility and comparable low cost. Moreover, they should also possess good film forming ability and an appropriate morphology. Furthermore, cellulose acetate polymers are very convincing, with characteristics such as good toughness (Kesting 1985) good desalting, moderate flux (Bokhorst 1981) and relatively low cost (Brandt et al 1993). Many studies have proven that cellulose acetate is highly comparable to other synthetic polymer materials as well as effective in ultrafiltration process (Arthanareeswaran et al 2004; Nigmatullin et al 1990; Sajitha et al 2002; Ye et al 2002).
Polymer blending is a possibility of modifying membrane material properties such as pore statistics, hydrophilicity and morphological structure. A blend can show new properties not found for single polymers. This also holds for membrane preparation to tailor a specific separation performance. The blends contain the separate polymers as individual domains or phases (Camargo et al 1991). Blends often consist of a matrix of one polymer containing another polymer as a dispersed or cocontinuous phase. Several authors have studied the role of blending on the performance of the resultant membranes. Rahimpoure et al (2007) has studied the blending behavior of PES with cellulose acetate phthalate (CAP) and reported that the performance of pure water flux increases initially and further addition of CAP sharply decreases the membrane performance. Bowen et al (2001) has reported the effect of addition of sulfonated polyetheretherketone (SPEEK) in polysulfone membrane. Malaisamy et al (2002) has studied the effect of additive on blend membrane of cellulose acetate.

The performance of the membranes could be improved and membranes with wide range of pore size and morphology are prepared by employing hydrophilic materials in the casting solution. Thus, the mixer of PVA and gelatin was believed to be compatible with the polymers polyethersulfone, cellulose acetate, polysulfone etc., for ultrafiltration membrane preparation (Pal et al 2007; Michon et al 1995; Pal et al 2006). Membrane characteristics and solution parameters are paramount importance in selection of membrane for a specific application. Various characteristics of the membranes have been studied in detail, by many of the researchers, of which compaction, pure water flux, membrane hydraulic resistance, molecular weight cut-off (MWCO), pore statistics are found to have primary importance. The effect of compaction on water flux of ultrafiltration membranes have been studied by Persson et al (1995). Pore statistics has been studied by Capannelli et al (1983) and MWCO by Abaticchio et al (1990). Membranes have also been
used for concentration of proteins such as BSA and enzymes such as cytochrome and lysozyme etc. (Grund et al; 1992; Ghosh and Cui 2000).

Though there are several reports on the improvement of properties and performance of cellulose acetate using blending with organic (Bowen et al 2001), inorganic (Choi et al 2006) and additives (Arthanareeswaran et al 2004), there is no much report on fouling studies. Hence, to develop ultra filtration membranes with improved properties, for desired application, attention has been focused in the present investigation to modify cellulose acetate with a biopolymer. Further, the modified membranes were characterized for their UF properties including fouling. The membrane fouling was studied by adding various composition of PVA/gelatin mixing pair in the base cellulose acetate polymer. A mathematical model was also been developed for predicting the gel layer concentration as well as polarized layer resistance for the prepared membranes.

1.3.1 Membrane Classification

The membranes used for separation process are classified in the following aspects:

- According to morphology
- According to separation mechanisms
- According to driving forces

In general, there are two classes of membrane morphologies, (Mulder 1991; Arthanareeswaran 2007) symmetric and asymmetric membranes and their cross sectional views are shown in Figures 1.3 and 1.4. The symmetric membranes can further be subdivided into three groups of membranes.
Figure 1.3 Schematic illustrating of cross sections of symmetric and asymmetric membranes

Figure 1.4 (a) Schematic drawing of an asymmetric membrane and (b) Schematic drawing of a composite membrane
Homogeneous, dense membranes with an active layer thickness of more than 10 µm; these membranes are often used for the study of polymer material science aspects in gas separation and pervaporation. Cylindrical porous membranes which are normally used in small size laboratory experiments like enzyme and DNA separations from dilute solutions. Sponge-like porous membranes; these membranes have normally an average pore size of 0.2 - 5 µm and find application in the field of microfiltration. Bandala et al (2005) was developed homogeneous symmetric membrane for microfiltration application with cellulose acetate (CA) and activated carbon blend materials. Further, the asymmetric membranes can also be subdivided into three groups:

1. Porous membranes; here, the membrane does not have the same pore size over the whole membrane thickness but a pore size gradient.

2. Porous membranes having a top layer; these laid membranes normally have a top open smaller porous layer, over a second layer with much bigger pores (5-500 nm). Membranes of this type, i.e., integrally skinned asymmetric membranes are generally used in ultrafiltration applications.

   Integrally skinned asymmetric membranes has been reported by Arthanareeswaran et al (2007) using CA and polyvinylpyrrolidone polymers for ultrafiltration application.

3. Composite membranes; a homogeneous layer is placed in a second production step on top of a support membrane. Integrally-skinned and composite membranes for the separation of gases and liquids (pervaporation) have selective layers thinner than 1 µm.
Most ultrafiltration (UF) membranes have an asymmetric structure (Broens 1980; Smolders 1992), they are porous with a porous top layer. Both polymers and inorganic materials are used for the preparation of membranes. Polymeric UF membranes are very often prepared by the immersion precipitation process. For this purpose, a solution of the polymer is cast as a thin film, and immersed in a coagulation bath that contains a non solvent and solvent for the polymer and surfactant agents. Solvent starts to diffuse out of the homogeneous liquid polymer film, whereas non-solvent diffuses into the film. Due to the presence of the non-solvent, phase inversion takes place in the polymer film and the polymer precipitates as a solid phase to form a porous asymmetric membrane structure. More detailed information about membrane preparation techniques are available in literature (Mulder et al 1991).

1.3.2 Classification according to separation mechanisms

According to the mechanism of separation, the membranes are classified mainly in to eight categories such microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), gas separation, pervaporation and facilitated transport.

1.3.3 Classification according to driving forces

The driving forces are such as pressure, concentration, temperature and energy a general overview of membrane driving forces and mechanism are presented in the Tables 1.1 and 1.2.
Table 1.1  Overview of membrane processes, driving force, separation mechanism, and states of feed and permeate

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Driving force</th>
<th>Feed state</th>
<th>Permeate state</th>
<th>Separation mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration (MF)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Size</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Size</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Size/ Affinity</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Size/ Affinity</td>
</tr>
<tr>
<td>Piezodialysis (PD)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Affinity</td>
</tr>
<tr>
<td>Gas separation (GS)</td>
<td>ΔP</td>
<td>Gas</td>
<td>Gas</td>
<td>Affinity/ Size</td>
</tr>
<tr>
<td>Pervaporation (PV)</td>
<td>ΔP</td>
<td>Liquid</td>
<td>Gas</td>
<td>Affinity</td>
</tr>
<tr>
<td>Dialysis (D)</td>
<td>Δc</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Size</td>
</tr>
<tr>
<td>Osmosis (O)</td>
<td>Δc</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Affinity</td>
</tr>
<tr>
<td>Liquid membranes (LM)</td>
<td>Δc</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Chemical nature</td>
</tr>
<tr>
<td>Electrodialysis (ED)</td>
<td>ΔE</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Charge</td>
</tr>
<tr>
<td>Membrane distillation (MD)</td>
<td>ΔT, ΔP</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Vapour pressure</td>
</tr>
</tbody>
</table>

Table 1.2  Comparison of pressure-driven membrane processes

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Pore size (nm)</th>
<th>Material retained</th>
<th>Material passed</th>
<th>Pressure (bar)</th>
<th>Type of membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>&gt; 50</td>
<td>Particles (bacteria, yeasts etc)</td>
<td>Water, salts macromolecules</td>
<td>&lt; 2</td>
<td>Porous</td>
</tr>
<tr>
<td>UF</td>
<td>1 – 100</td>
<td>Macromolecules, water, colloids, lattices solutes Mw &gt; 10,000</td>
<td>Water, salts and sugars</td>
<td>1-10</td>
<td>Microporous</td>
</tr>
<tr>
<td>NF</td>
<td>≈1</td>
<td>Solutes Mw &gt; 500, di- and multivalent ions</td>
<td>water, sugars, monovalent ions</td>
<td>5-20</td>
<td>Microporous</td>
</tr>
<tr>
<td>RO</td>
<td>Not relevant</td>
<td>All dissolved and suspended solutes (salts, sugars)</td>
<td>Water</td>
<td>15-80</td>
<td>Nonporous</td>
</tr>
</tbody>
</table>
1.4 MEMBRANE MATERIALS

The materials used for preparing membrane material will be of either organic or inorganic in nature the schematic floe diagram is as shown in Figure 1.5.

![Schematic flow diagram of classification of membrane materials](image)

**Figure 1.5** Schematic flow diagram of classification of membrane materials

1.4.1 Requirement as membrane materials

If the membrane material is said to be good, then the materials should have the following properties:

- process ability (membrane forming properties)
- chemical stability (solvents, solutes, oxidation)
- mechanical stability
- thermal stability
- hydrophilicity / hydrophobicity (wetting)
- adsorption (fouling)
- biocompatibility

A polymer membrane should

- Be capable of forming films
- Posses mechanical strength
- Posses hydrophilicity / hydrophobicity (wetting)
- Demonstrate chemical stability over a range of pH

1.4.2 Membrane fabrication

During the last few decades of intensive membrane preparation research, different techniques have been proposed to generate selective, permeable films. The porous membranes may be prepared either by sintering or stretching or track etching or phase inversion processes. The most used and thus important class of techniques is called phase inversion techniques. These processes rely on the phase inversion of polymer solutions producing porous polymer films. Often these structures can act as a membrane. Membranes are fabricated by Sintering, Stretching, Track-etching, Template Leaching, Coating and solution casting by phase inversion. Ultrathin alumina hollow fibers microfiltration membranes were prepared by a sintering method (Choi et al 2006). The porous track etched membrane has been fabricated in the micro and ultrafiltration range 15 to 100 nm with polycarbonate polymer materials (Yamazaki et al 1996). Porous polyethylene membranes were successfully prepared by the template-leaching technique. The leachable
component was tapioca starch, which was compounded with low-density polyethylene (LDPE) to produce a blend percentage of 2, 4, 6, 8, 10, or 12% by weight of starch material (Nguanruksa et al 2004). The microporous membrane based on poly(vinylidene fluoride) (PVdF) is prepared with phase inversion method. In addition to phase inversion process, solvent pre-evaporation and uni-axial stretching processes were introduced to enhance tensile strength and ionic conductivity of the membrane (Seol et al 2006).

1.4.3 Polymeric materials as membrane

The polymeric material is considered to be an ideal for membrane preparation and membrane separation that involves extreme process conditions. Most of the membranes can be prepared from either organic or inorganic materials. Hence, polymer membranes are effectively employed when compared with membranes prepared from other materials (Table 1.3).

In order to be a suitable material for use as a membrane, a polymer must possess good film-forming properties. The resulting film must have some degree of permeability as well as allowing preferential transport of selected components of a solution. Membrane performance characteristics have been reported for various solvents, casting solution compositions, and casting conditions (Tweddle et al 1983). Additives such as Poly-(N-vinylpyrrolidone) (PVP) are frequently included in the casting formulation to alter the behavior of the casting solution and, as a consequence, the membrane structure. This type of approach has been described by Lafreniere et al (1987) and Miyano et al (1990).
Table 1.3  Comparison of membrane materials for membrane separation processes

<table>
<thead>
<tr>
<th>Feature</th>
<th>Microfiltration</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
<th>Reverse Osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td>Ceramics, sintered metals, polypropylene, polysulfone, polyethersulfone, polyvinylidene fluoride, poly tetrafluoroethylene</td>
<td>Ceramics, sintered metals, cellulosics, polysulfone, polyethersulfone, polyvinylidene fluoride</td>
<td>Thin film composites, cellulosics</td>
<td>Thin film composites, cellulosics</td>
</tr>
<tr>
<td>Poresize Range (µm)</td>
<td>0.01 - 1.0</td>
<td>0.001 - 0.01</td>
<td>0.0001 - 0.001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Mol. Wt Cut off Range (Dalton)</td>
<td>&gt;100,000</td>
<td>2,000 - 100,000</td>
<td>300 - 1,000</td>
<td>100 - 200</td>
</tr>
<tr>
<td>Operating Pressure Range</td>
<td>&lt;30</td>
<td>20 - 100</td>
<td>50 - 300</td>
<td>225 - 1,000</td>
</tr>
<tr>
<td>Suspended Solids Removal</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Dissolved Organics Removal</td>
<td>None</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Dissolved Inorganics Removal</td>
<td>None</td>
<td>None</td>
<td>20-85%</td>
<td>95-99%</td>
</tr>
<tr>
<td>Microorganism Removal</td>
<td>Protozoan cysts, algae, bacteria</td>
<td>Protozoan cysts, algae, bacteria</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>Osmotic. Pres Effects</td>
<td>None</td>
<td>Slight</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Concentration Capabilities</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Permeate Purity</td>
<td>High</td>
<td>High</td>
<td>Moderate-high</td>
<td>High</td>
</tr>
<tr>
<td>Energy Usage</td>
<td>Low</td>
<td>Low</td>
<td>Low-moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Membrane Stability</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
1.5 ULTRAFILTRATION MEMBRANES

The term “ultrafiltration” (UF) has been introduced by Bechold (1907), to discriminate this process from separation by filtration, where much larger particles are separated (> 1 μm). The ultrafiltration membrane process, which was initially developed for the treatment of wastewaters and sewage, is now widely used in various applications in industries such as automobile (electrocoat paint), food and dairy (sugar refining, vegetable oils, corn, fruit juices, wine and beer, fluid milk, cheese and whey) and biotechnology (enzyme recovery, membrane bioreactors) industries. A detailed review of such applications have been done by Cheryan et al (1998).

Many polymers have been used for ultrafiltration (UF) membrane material such as cellulose acetate (CA), poly-acrylonitrile (PAN), polyethersulfone (PES), polysulfone (PS) and polyamide (Chen et al 2009; Rahimpour and Madaeni 2007; Bowen et al 2001; Hosch and Staude 1996). In case of UF membranes, the polymer material should exhibit excellent biocompatibility and comparable low cost. Moreover, they should also possess good film forming ability and an appropriate morphology. Amongst these polymeric materials, cellulose acetate has always been used as the basic material for UF membranes with their maximum uniformity, perm selectivity and optimum physical properties such as strength and flexibility. Furthermore, cellulose acetate polymers are very convincing, with characteristics such as good toughness (Kesting 1985) good desalting, moderate flux (Bokhorst 1981) and relatively low cost (Brandt et al 1993). Many studies have proven that cellulose acetate is highly comparable to other synthetic polymer materials as well as effective in ultrafiltration process (Arthanareeswaran et al 2004; Nigmatullin et al 1990; Sajitha et al 2002; Ye et al 2002).
1.5.1 Ultrafiltration membrane fabrication by phase inversion method

Phase inversion mechanisms can generally be subdivided into five main categories such as precipitation in a non-solvent (typically water), non-solvent induced (NIPS), precipitation by absorption of non-solvent (water) from the vapor phase, vapour induced (VIPS), solvent evaporation, evaporation induced (EIPS), precipitation by cooling thermally induced (TIPS). By posing a change in one of these parameters such as temperature, activity of polymer and solvent at one particular side of the film, asymmetric boundaries are posed on the polymer film and resulting in the derived structure. For example, a change in the temperature at the interface of the polymer solution, heat will be exchanged and demixing can be induced and is known as temperature induced phase separation (Blanco 2006), TIPS. The original polymer solution can also be subjected to a reaction, which causes phase separation and is known as reaction induced phase separation, RIPS. The most used technique is based on diffusion induced phase separation, DIPS in which a polymer solution is allowed to contact with non-solvent vapour, air or non solvent liquid, and is illustrated in Figure 1.6. Thus, diffusional mass exchange will lead to a change in the local composition of the polymer film and demixing can be induced.

When a polymer is subjected to a vapor containing a non solvent (a species not miscible with the polymer), often symmetric structures are generated. Membrane formation by evaporation (porous structures) uses polymer solutions containing a volatile solvent, a less volatile non solvent and a polymer. Preferential loss of solvent will generate meta- or unstable compositions and phase separation will be induced at this point. Immersion precipitation is achieved by diffusion of non solvent from a coagulation bath into the polymer film and diffusion of solvent from the polymer solution into
the nonsolvent bath. An appropriate amount of the polymer solution was dispersed uniformly on a glass plate and then immersed immediately into a coagulation bath to induce precipitation. The coagulation bath consisted of pure water or volatile solvent/water (nonsolvent) solutions.

**Figure 1.6** Schematic representations of three DIPS processes

A) Precipitation with nonsolvent vapor, B) Evaporation of solvent and C) Immersion precipitation. Main direction of diffusion of the different species is indicated by arrows. Polymer, solvent and nonsolvent are represented with P, S and NS respectively. Components which are not necessary to be present in the original polymer solution and coagulation bath are put between brackets.

1.6 MODIFICATION OF POLYMER FOR MEMBRANE MATERIALS

Modification of the membrane material/surface to increase hydrophilicity or modify the surface charge has been investigated for reducing adsorption/fouling of UF membranes. The techniques investigated for this purpose includes, co-polymerization of monomer/copolymers, blending of hydrophilic or charged polymers with hydrophobic polymers.
1.6.1 General modification methods

The general modification methods to get new kind of polymer membranes are, surface/physical modification, grafting and blending. In surface modification the hydrophilic groups have the opportunity to be linked on the polymer membrane. The grafting technique incorporates the hydrophilic polymers are joined onto the hydrophobic surface of polymer membrane by using UV light radiation and heat to initiate graft polymerization. The most common way to modify the membrane material is blending method in this there is an advantage of the two polymers could be endowed to the blend membrane obtained by casting blend solutions of base and other blending polymers.

Usually, modifications of the polymer structure by introducing polar (or) ionic groups, which are intended to change the surface charge characteristics, also increase the polymer hydrophilicity. Cellulose acetate is a widely used material for UF membranes because of its relatively good thermal/chemical stability and processibilty. Similarly, the natural polymer like gelatin and polyvinyl alcohol, those are having high hydrophilic nature and anti fouling behavior can be used with CA (Pal et al 2007) and other polymers like PES and PSf.

1.6.2 Modification by blends

Blending of a miscible hydrophilic polymer with a chemically or thermally stable hydrophobic polymer has been investigated (Yoo 2003) for achieving stable polymeric materials with improved hydrophilicity. However, the choice of polymers is limited since only a few polymers form homogeneous blends (Krause 1978). Polyvinylpyrrolidinone (PVP), a hydrophilic polymer is known to form blends with polysulfone (Tam et al 1993), poyethersulfone, polyimide, and polyetherimide (Roesink 1989).
Membranes from homogeneous blends of these polymers can be prepared by phase inversion. Chen et al (1996) have prepared mechanically stable, partially charged hydrophilic membranes from blends of aminated polysulfone or sulfonated polysulfone with polysulfone.

Polymer blends have provided an efficient way to fill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced performances and antifouling behavior. The great majority of useful blends are immiscible, and in these blends, mechanical properties can be optimized by controlling the blend morphology (Sundararaj and Macosko 1995). The synthesis of a polymer blend membrane is motivated by the desire to superimpose requisite properties upon the transport properties of a base polymer (Sivakumar et al 1996). Polymer blending is a possibility of modifying membrane material properties such as pore statistics, hydrophilicity and morphological structure. A blend can show new properties not found for single polymers. This also holds for membrane preparation to tailor a specific separation performance. It is well known that many polymers do not mix on a molecular level. The blends contain the separate polymers as individual domains or phases (Camargo et al 1991). Blends often consist of a matrix of one polymer containing another polymer as a dispersed or co-continuous phase. Several authors have studied the role of blending on the performance of the resultant membranes.

Rahimpour and Madaeni (2007) has studied the blending behavior of PES with cellulose acetate phthalate (CAP) and reported that the performance of pure water flux increases initially and further addition of CAP sharply decreases the membrane performance. Bowen et al (2001) has reported the effect of addition of sulfonated polyetheretherketone (SPEEK) in polysulfone membrane. Malaisamy et al (2002) have studied the effect of
additive on blend membrane of cellulose acetate/sulfonated polysulfone and reported the effect of additive on polymer blends by pure water flux, membrane hydraulic resistance and rejection.

1.6.3 Modification of polymer with biomaterials

Most of the conventional materials do not meet the demands required for both their surface and bulk properties when used as biomaterials. An effective approach for developing a clinically applicable biomaterial is to modify the surface of the material which already has excellent bio functionality and bulk properties. This thesis focuses on the surface modification of polymers by blending (Ranaa 2005), which have long been known in physical mixing in polymer chemistry but are not yet widely applied to biomaterials. Amiji (1995) was developed chitosan-poly (ethylene oxide) (PEO) blend membranes, using different molecular weights of PEO, for improved permeability and blood compatibility. Other researcher (Zeng et al 2004) was reported the blending of chitosan with two synthetic polymers, e.g. polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) to prepare microporous chitosan membrane.

Polyvinyl alcohol (PVA) blends have long been used with other natural polymers because of PVA’s ability to form films (Valdir 2004). The performance properties of PVA are influenced by the molecular weight and the degree of hydrolysis of gelatin which is also used as blending material is obtained by the thermal denaturation of collagen from animal skin, bones, and, rarely, fish scales. It contains mainly the residues of 3 amino acids glycine (arranged every third residue), proline, and 4-hydroxyproline in its structure. Gelatin contains extended left-handed proline helix conformations incorporated with 300 to 4000 amino acids. The gelling properties of the gelatin can be altered by the introduction of chemical cross-links by using transglutaminase to link lysine to glutamine residues or glutaraldehyde to
link lysine to lysine. The mixing of PVA with gelatin possesses a film-forming property. Accordingly, it is used for making hard and soft gelatin capsules. Considering the film-forming property, a PVA-gelatin film was thought to be a good candidate for artificial skin. Hence, attempts were made to develop a modified membrane by esterifying the hydroxyl group of PVA with the carboxyl group of gelatin and mixed with cellulose acetate to get new kind of ultrafiltration membrane.

The performance of the membranes could be improved and membranes with wide range of pore size and morphology are prepared by employing hydrophilic materials in the casting solution. Thus, the mixer of PVA and gelatin was believed to be compatible with the polymers polyethersulfone, cellulose acetate, polysulfone etc., for ultrafiltration membrane preparation (Pal et al 2007; Michon et al 1995; Pal et al 2006). Membrane characteristics and solution parameters are paramount importance in selection of membrane for a specific application. Various characteristics of the membranes have been studied in detail, by many of the researchers, of which compaction, pure water flux, membrane hydraulic resistance, molecular weight cut-off (MWCO), pore statistics are found to have primary importance. The effect of compaction on water flux of ultrafiltration membranes have been studied by Persson et al (1995). Pore statistics has been studied by Capannelli et al (1983) and MWCO by Abaticchio et al (1990). Membranes have also been successfully used for concentration of proteins such as BSA and enzymes such as cytochrome and lysozyme etc. (Grund et al 1992; Ghosh Cui 2000).

Though there are several reports on the improvement of properties and performance of cellulose acetate using blending, the use of PVA/gelatin pair with CA is not available. Hence, to develop UF membranes with improved properties and for desired application, attention has been focused in
the present investigation to modify cellulose acetate with a biopolymer, gelatin along with PVA. Further, the modified membranes were characterized for their UF properties. The membrane fouling was studied by adding various composition of PVA/gelatin mixing pair in base CA polymer. A mathematical model was also been developed for predicting the gel layer concentration as well as polarized layer resistance for the prepared membranes.

1.7 MEMBRANE MODULES AND CONFIGURATIONS

Since the introduction of membrane treatment technology back in the 1970's, a variety of membrane types and configurations have been developed. The types of ultrafiltration modules commercially prepared are:

- Flat sheet membrane
- Tubular membrane modules
- Spiral wound membrane modules
- Hollow fibre membrane elements

The immersion type flat membrane module operates suction or gravity filtration while the membrane is being rinsed by aeration. Tubular membranes are based on either PVDF (polyvinylidene fluoride) or PSf (polysulfone), polyethersulfone. They are capable of continuous, reproducible processing cycles, which means they are cleanable, durable, easy to operate and a proven advance in technology. Spiral wound membrane technology was first introduced more than 30 years ago. Some of the many applications that employ the spiral wound membranes are Seawater desalination, Brackish Water treatment and Recovery of High purity water production, Dairy processing, Whey protein concentration. Hollow fiber membranes have been successfully employed in a wide variety of industries including food, juice, pharmaceutical, metal working, dairy, wine and most recently municipal
drinking water. Depending on the application, hollow fiber membranes can be highly practical and cost effective alternatives to conventional chemical and physical separation processes.

1.8 CHARACTERIZATION OF MEMBRANES

The characterization of the membranes is essential in order to enhance their performance in the separation and technology processes. Membranes were characterized in terms of compaction, pure water flux, water content, membrane resistance, molecular weight cut-off (Causseranda 2002) and morphological studies. The pore sizes of the membranes play an important role in deciding the type and performance of membranes. Since membrane performance is governed by its characterization, many attempts were made on characterization of membranes. The necessity and effect of compaction on the water flux of ultrafiltration membranes have been studied by Persson et al (1995). The effect of various concentrations of additives on the formation and performance of polyethersulfone ultrafiltration membranes in terms of water permeability and solute rejection has been studied in detail by Chaturvedi et al (2001) and Khan et al (2000).

Kim et al (1990) examined the effect of the density of the hydrophilic group on the pure water flux and water content of membranes. The change in flux was elucidated by considering pore volume change and the site of graft chains. The membrane performance was evaluated by the water flux and the rejection of dextran using polyacrylonitrile ultrafiltration membranes by Nouzaki et al (2002). Johnson and Johnson (1995) determined the water flux for hydrophobic/hydrophilic ultrafiltration membranes with increasing time. Mulder (1991) concluded that membrane compaction would lead to a denser structure with smaller pores. Transmembrane flux and membrane solute retention are determined in filtration tests. Transmembrane flux is generally measured as a function of applied hydrostatic pressure with
ultra-pure water. Molecular weight of the polymer and the casting solution composition could affect the pore size and pore size distribution on the surface of the resulting membrane (Nguyen et al 1980).

The performance of ultrafiltration and microfiltration is an important role and determined by deposition of protein layer (Opong and Zydney 1990). The hydraulic permeability of the protein deposit decreased with increasing the filtration pressure. Water content is directly dependent on the porosity of membranes and an index of membrane hydrophilicity and flux and studied by Prabhakar and Misra (1986), Tamura et al (1981) and also by Mohan group, Mahendran et al (2004), Arthanareeswaran et al (2004a).

The molecular weight cut-off (MWCO) was constructed by measuring the separation values of polyethylene glycol solutes of varying molecular weights. The method for determining the concentration of polyethylene glycol was given by Sabde et al (1997).

Based on the survey of literature, it was decided to systematically characterize the membranes in terms of compaction, pure water flux, membrane hydraulic resistance by measuring the pure water flux of the membranes at different transmembrane pressures, water content, molecular weight cut-off by using globular proteins of varied molar masses as solute probes and membrane morphology by scanning electron microscopy.

1.9 SEPARATION OF BIO MOLECULES BY UF MEMBRANE PROCESS

The rapid growth in the field of biotechnology has led to an increase in the demand for efficient, large-scale protein rejection processes. The major advantage of ultrafiltration processes over conventional processes is high throughput of product. Fane et al (1983) explained ultrafiltration of
proteins through partially-permeable membranes. The flux and rejection are time-dependent, flux shows an initially rapid and then a more gradual decline that is attributable to loss of porosity by internal adsorption followed by surface adsorption.

Iritani et al (2002) examined the dynamic behavior of dead-end ultrafiltration of dilute aqueous BSA protein solution. The concentration distributions in the filter cake, accumulated on the membrane surface in dead-end ultrafiltration of protein solutions, were measured using the principle of inclined ultrafiltration where a large amount of filter cake is formed. Balakrishnan and Agarwal (1996) concluded that a high degree of protein separation is generally obtained at low fluxes, corresponding to low transmembrane pressures.

Dynamic ceramic ultrafiltration membrane was characterized in terms of ovalbumin protein solution, the linear velocity along the membrane, bulk protein concentration, pressure and pH in the feed solution were studied in detail by Matsuyama et al (1994). In various industrial fields, such as food and medical industries and bio industry, it becomes increasingly important to separate solution constituents such as proteins, enzymes, antibodies, hormones, and blood proteins (Nakao et al 1988). Magueijo et al (2002) have reported protein ultrafiltration (UF) and its dependence on UF operating conditions. Cellulose acetate (CA) asymmetric membranes are made in laboratory by the phase-inversion method and characterized in terms of pure water permeability and molecular weight cut-off (MWCO) (10000 Da for 98% of rejection). Permeation experiments were carried out for solutions of reference solutes in order to characterize the membranes and for lysozyme solutions under different operating conditions. The influence of the ionic strength in the permeation flux and protein rejection is studied by performing
permeation tests with a solution of lysozyme (0.3 kg/m$^3$) containing different NaCl concentrations.

The transmission of the major chicken egg with proteins i.e., ovalbumin and conalbumin, were found to depend on the transmembrane pressure; transmission decreased with increase in transmembrane pressure (Gosh et al 2001). Mukai et al (1998) have conducted ultrafiltration of mixtures of bovine serum albumin and egg white lysozyme using membranes which were almost completely retentive for BSA but permeable for lysozyme. Chiang et al (1993) have reported a two-step process involving diafiltration and affinity separation for purification of lysozyme.

The contributions of individual protein species to the apparent critical flux were evaluated as well as the separation performance by Ghan et al (2002). For mixtures of globulin/lysozyme and BSA/lysozyme the larger retained protein tended to control the critical flux behaviour. Causseranda et al (2002) determined the apparent MWCO of ultrafiltration membranes using a mixture of dextran protein solutions. Tests were conducted with a flat-sheet membrane with an effective filtration area.

1.10 MEMBRANE FOULING

The membrane surface free energy (and which is related to the property hydrophilicity/hydrophobicity) influences membrane particle adsorption or fouling phenomena. In most membrane separation processes (especially bioseparations), higher surface hydrophilicity corresponds to the lower fouling. Synthetic membrane fouling impairs membrane performance has studied by Zeaman et al (1996). As a consequence, a wide variety of membrane cleaning techniques has been developed. Sometimes fouling is irreversible, and the membrane needs to be replaced.
The flux through the membrane decreases slowly with time in all the membrane process due to fouling caused by a variety of factors such as slime formation, microbial growth, and deposition of macromolecules, colloid deposition and physical compaction of the membrane. Fouling is irreversible and necessitates the replacement of the membrane. The fouling behavior can be inhibited by

- Careful selection of the membrane material.
- Pretreatment of feed (such as PH adjustment or precipitation to remove salt).
- Frequent cleaning of the membrane with chemicals.
- Back flushing with permeate

1.10.1 Concentration polarization and membrane fouling

A key factor determining the performance of ultrafiltration membranes is concentration polarization (Redkar et al 1996), which causes membrane fouling due to deposition of retained colloidal and macromolecular material on the membrane surface. The pure water flux of ultrafiltration membranes is often very high i.e. greater than 1 cm$^3$/cm$^2$ min (350 gal/ft$^2$ day). However, when membranes are used to separate macromolecular or colloidal solutions, the flux falls within seconds, typically to 0.1 cm$^3$/cm$^2$ min. This immediate drop in flux is caused by the formation of a gel layer of retained solutes on the membrane surface due to concentration polarization (Xinghua et al 2008). This gel layer forms a secondary barrier to flow through the membrane. This first decline in flux is determined by the composition of the feed solution and its fluid hydrodynamics. Sometimes the resulting flux is constant for a prolonged period, and when the membrane is retested with pure water, its flux returns to the original value. More commonly, however, a further slow decline in flux occurs over a period of
hours to weeks, depending on the feed solution. Most of this second decrease in flux is caused by slow consolidation of the secondary layer formed by concentration polarization on the membrane surface (Gill et al 1988). Formation of this consolidated gel layer, called membrane fouling, is difficult to control. Control techniques include regular membrane cleaning, back flushing, or using membranes with surface characteristics that minimize adhesion. Operation of the membrane at the lowest practical operating pressure also delays consolidation of the gel layer.

If the regular cleaning cycle repeated many times, the membrane flux eventually does not return to the original value on cleaning. Part of this slow, permanent loss of flux is believed to be due to precipitates on the membrane surface that are not removed by the cleaning procedure. A further cause of the permanent flux loss is believed to be internal fouling of the membrane by material that penetrates the membrane pores and becomes lodged in the interior of the membrane. Ultrafiltration membranes are often used to separate colloids from water and micro solutes. In this case the tendency is to use relatively high-molecular-weight cut-off membranes, but the higher fluxes of these membranes can be transitory because they are more susceptible to internal fouling. A membrane with a lower molecular weight cut-off, even though it may have a lower pure water flux, often provides a more sustained flux with the actual feed solutions because less internal fouling occurs.

As described above, the initial cause of membrane fouling is concentration polarization, which results in deposition of a layer of material on the membrane surface. In ultrafiltration, solvent and macromolecular or colloidal solutes are carried towards the membrane surface by the solution permeating the membrane.
Solvent molecules permeate the membrane, but the larger solutes accumulate at the membrane surface. Because of their size, the rate at which the rejected solute molecules can diffuse from the membrane surface back to the bulk solution is relatively low. Thus their concentration at the membrane surface is typically 20–50 times higher than the feed solution concentration. These solutes become so concentrated at the membrane surface that a gel layer is formed and becomes a secondary barrier to flow through the membrane.

1.10.2 Membrane cleaning

Several cleaning methods are used to remove the densified gel layer of retained material from the membrane surface. The easiest is to circulate an appropriate cleaning solution through the membrane modules for 1 or 2 h. The most common ultrafiltration fouling layers are organic polymer colloids and gelatinous materials are best treated with alkaline solutions followed by hot detergent solutions. Enzymatic detergents are particularly effective when the fouling layer is a proteinaceous gel. Calcium, magnesium, and silica scales, often a problem with reverse osmosis membranes, are generally not a problem in ultrafiltration because these ions permeate the membrane (ultrafiltration of cheese whey, in which high calcium levels can lead to calcium scaling, is an exception). Because many feed waters contain small amounts of soluble ferrous iron salts, hydrated iron oxide scaling is a problem. In the ultrafiltration system these salts are oxidized to ferric iron by entrained air. Ferric iron is insoluble in water, so an insoluble iron hydroxide gel forms and accumulates on the membrane surface. Such deposits are usually removed with a citric or hydrochloric acid wash. Regular cleaning is required to maintain the performance of all ultrafiltration membranes. The period of the cleaning cycle can vary from daily for food applications, such as ultrafiltration of whey, to once a month or more for ultrafiltration membranes.
used as polishing units in ultrapure water systems. A typical cleaning cycle is as follows:

1. Flush the system several times with hot water at the highest possible circulation rate.

2. Treat the system with an appropriate acid or alkali wash, depending on the nature of the layer.

3. Treat the system with a hot detergent solution.

4. Flush the system thoroughly with water to remove all traces of detergent; measure the pure water flux through the membrane modules under standard test conditions. Even after cleaning, some degree of permanent flux loss over time is expected. If the restoration of flux is less than expected, repetition of steps 1-3 is needed.

Because of the challenging environment in which ultrafiltration membranes are operated and the regular cleaning cycles, membrane lifetime is significantly shorter than that of reverse osmosis membranes. Ultrafiltration module lifetimes are rarely more than 2-3 years, and modules may be replaced annually in cheese whey or electro coat paint applications. In contrast, reverse osmosis membranes are normally not cleaned more than once or twice per year and can last 4-5 years.

1.11 MATHEMATICAL MODELS OF ULTRAFILTRATION

In ultrafiltration of a solution, however some other resistances add to membrane resistance causes flux decline. There are several models developed to predict the performance of ultra filtration, but most of them developed to predict the effect of concentration. Examples are film polarization model, gel-layer polarization model, gel-polarization model,
boundary layer resistance model, osmotic pressure model. The models are described below.

1.11.1 Cake filtration model in a non-stationary process

The filtration model in the non-stationary process (relaxation model) uses the mass transport balance equation during membrane filtration in which the decrease in the permeate flux \( J \) is proportional to its value.

\[
\frac{d}{dx}(J - J_0) + \frac{1}{t_0}(J - J_\infty) = 0 \tag{1.1}
\]

The solution for Equation (1.1) is for the following boundary condition for \( t = 0 \rightarrow J = J_0 \).

This model allows to calculating theoretical volume permeate flux over time.

\[
J_t = (J_0 - J_\infty) e^{-t/t_0} + J_\infty \tag{1.2}
\]

where \( J_t \) is the permeate flux after time equal \( t \). The model helps to calculate changes in the Permeate flux during the operation of the membrane modules, knowing only the initial flux \( (J_0) \), equilibrium fluxes \( (J_\infty) \) and time constant \( (t_0) \).

1.11.2 Hydraulic model of filtration resistance

The model is based on the equation which describes the correlation between permeate flux and pressure taking into account the hydraulic resistance fluid meets flowing through a membrane.
\[ J_t = \frac{\Delta P}{n(R_m + R_{rf} + R_{if})} \]  

(1.3)

where \( R_m \) is the membrane resistance, \( R_{rf} \) the resistance connected with reversible fouling \( R_{if} \) the resistance connected with irreversible fouling, \( n \) is fluid viscosity.

### 1.11.3 Thermodynamic model

The fundamental Staverman–Kedem–Katchalsky–Spiegler approach from the 1960’s is formulated in its current version as a local (at any point of a flat perm-selective membrane) set of equations for volume, \( J_V \), and solute, \( J_S \), fluxes (i.e. transport rates per unit area), which for a one-compound solution Spiegler (1996) is as follows:

\[ J_V = -l_p \left( \frac{dp}{dx} - \sigma RT \frac{dc}{dx} \right) \]  

(1.4)

\[ J_S = P_d \frac{dc}{dx} + (1 - \sigma)J_V C \]  

(1.5)

where \( C \) is the concentration of the solute, \( P \) the hydrostatic pressure, \( l_p \) the hydraulic permeability of the membrane, \( \sigma \) the Staverman reflection coefficient, \( R \) the gas constant, \( T \) the absolute temperature, and \( P_d \) is the diffusive permeability of the membrane.

### 1.11.4 Film polarization model

This model was developed based on the film theory and mass balance principle about the membrane. At steady state the convective flow through the membrane is balanced by solute flux through the membrane plus diffusive flow from the membrane (Jonsson 1984). Figure 1.7 shows the
concentration profile near the membrane surface (Gill 1984) at steady state from the feed side.

\[
\frac{dc}{dt} = J_v \frac{dc}{dx} + \frac{d}{dx} \left( D \frac{dc}{dx} \right) \tag{1.6}
\]

where \( C \) is the concentration at a distance \( x \) from the membrane surface.

\[D \frac{dc}{dx}\]

\[\text{Bulk concentration}\]

\[\text{Concentration boundary layer, } \delta\]

\[J_v C_p\]

\[J_v C_b\]

\[\text{C}_b\]

\[\text{X}\]

\[\text{C}_m\]

\[\text{Figure 1.7} \quad \text{Concentration profile near the membrane surface during steady state Ultra filtration}\]

The boundary conditions are \( X = 0 \) at \( C = C_m; X = \delta \) at \( C = C_b \)

where the boundary layer thickness is \( \delta \). \( C_b \) is the bulk solution concentration and \( C_m \) is the max value of the boundary layer concentration, which is the concentration at the membrane surface. Integrating the above equation gives

\[
J_v = k \ln \left( \frac{C_m - C_p}{C_b - C_p} \right) = D \delta \ln \left( \frac{C_m - C_p}{C_b - C_p} \right) \tag{1.7}
\]

where, \( D \) is the solute diffusion coefficient in the solvent, \( \delta \) is the thickness of the polarization layer and \( k \) is mass transfer coefficient.
1.11.5 Gel-Polarized model

The model applies to concentration polarization of non interacting particles in cross-flow filtration system.

\[ J_x = k \ln \frac{C_g - C_p}{C_b - C_p} \]  

(1.8)

\( C_g \) depends on the size, shape, chemical structure and degree of salvation of the solution. The \( C_g \) is given by

\[ C_g = C_p + (C_b - C_p) e^{j} \]  

(1.9)

The mass transfer coefficient appearing in the previous equation can be computed from the well known empirical correlation applicable for stirred cell:

\[ K = \phi (D / r)(v / D)^{0.33} (wr^2 / v)^{0.8} \]  

(1.10)

\( \phi \) is a module geometry dependent constant and can be experimentally determined for a given stirred cell unit as described by Opong and Zydney (1990). The \( \phi \) value was determined to be 0.343 and the diffusivity was calculated by using the following equation.

\[ D = 8.34 \times 10^{-8} (T / \mu w^{1/3}) \]  

(1.11)

Here \( D \) is in \( \text{cm}^2 \text{s}^{-1} \) and \( \mu \) is in \( C_p \) based on a molecular weight of and ambient operating conditions using dilute aqueous solution.
1.11.6 Osmotic pressure model

A concentration difference between two solutions, which are separated by a membrane, will cause an osmotic pressure difference (Vilker et al 1981). In order to create osmotic equilibrium, water is induced to flow from the low concentration region to the high concentration region. This reduces the convective flux generated by the operating transmembrane pressure. As any other flows in nature, the permeate flow across the membrane is governed by the free energy difference across the membrane. In addition, the coupling effect between water and solute may reduce this energy difference, and the effective transmembrane pressure may drop. Originally (Kedem and Katchalsky 1958), using irreversible thermodynamics, derived the relation:

\[ J_v = L_p (\Delta P - \sigma \Delta \pi) \]  

(1.12)

where \( J_v \) is the permeate flux, \( L_p \) is the membrane permeability, \( \Delta \pi \) is the osmotic pressure across the membrane \( [\Delta \pi = \pi (C_m) - \pi (C_p)] \) and \( \sigma \) is the reflection coefficient of solute across the membrane. The osmotic pressure effect on the permeate flux decline is scaled by the parameter \( \sigma \). The parameter measures the relative restriction of the membrane to transmit the solute compared to the solvent, and varies between 0 for a freely permeable to 1 for a completely impermeable solute. \( L_p \) is an inverse function of membrane resistance which includes both membrane and fouling resistance due to adsorption.

Therefore the equation for permeate flux is given by equation (1.13)

\[ J_v = \frac{\Delta P - \sigma \Delta \pi}{\mu_i (R_m + R_f)} \]  

(1.13)
$R_f$ is assumed to be independent of pressure and stands to account for the effect of adsorption.

### 1.11.7 Resistances-in-series model

The model has been used to predict the performance of ultrafiltration of different macromolecule solutions. This model considers all the resistances involved in flux decline such as membrane resistance, adsorption resistance, pore blockage resistance concentration polarization resistances in series. Permeate flux can be given by equation (1.13) Where,

$$J_v = \frac{\Delta P}{\mu(R_m + R_a + R_c)}$$  \hspace{1cm} (1.14)

where $J_v$ is permeate flux, $\mu$ is viscosity, $R_a$ is absorption resistance, $R_m$ is membrane resistance, $R_c$ polarized layer resistance.

Where Membrane resistance

$$R_m = \frac{\Delta P}{\mu J_0}$$  \hspace{1cm} (1.15)

and Polarized resistance is given by

$$R_c = \frac{\Delta P}{\mu J} - R_m - R_a$$  \hspace{1cm} (1.16)

where $J$ is denotes the permeate flux and the total resistance is equals first membrane resistance.

### 1.11.8 Kinetic model representing pore blocking

The deposition mechanism on the membrane surface and into its porous structure was analyzed in terms of various kinetic models, viz., cake filtration, standard blocking and complete pore-blocking models. It was seen
that an initial intense flux decline due to external blockage followed by the formation of a cake. The kinetic model by Hermia et al is given by

$$\frac{d^2t}{dV^2} = K \left( \frac{dt}{dV} \right)^{\beta}$$

(1.17)

The \( \beta \) value represents the nature of fouling, theoretically defined values and type of fouling is given by blocking filtration laws, if \( \beta \) value is less than 0 then it is cake filtration with compression and if it is equal to 0, 1 and 2 then cake filtration, intermediate blocking and complete blocking will take place respectively.

The equation (1.17) is integrated to give it in general form by

$$\frac{t}{V} = [K(l - \beta)]^{\frac{1}{1-\beta}} \cdot (V)^{\frac{1}{1-\beta}}$$

(1.18)

From the above equation \( t/V \) vs \( v \) gives the \( \beta \) value which represents the nature of filtration.

From the above literature survey we conclude that Flat sheet module is used for membrane preparation by phase inversion process as flat sheet module can be easily removed for cleaning and replacement of defective membranes. Ultra filtration is used for the separation process as ultra filtration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. Low applied pressures are therefore sufficient to achieve high flux rates from an ultra filtration membrane. Gel polarized model is used for calculation of concentration polarization and resistance in series model is used as to calculate membrane resistance and polarized resistance and absorption resistance.
1.12 INDUSTRIAL APPLICATIONS OF ULTRAFILTRATION PROCESSES

The number of industrially relevant applications of ultrafiltration is very large. An overview of the most important applications is given by Cheryan (1986) and Kulkarni et al (1992). Some of these applications are summarized in 1.12.1.

1.12.1 Summary of important industrial applications of ultrafiltration processes

Environmental applications, such as waste water treatment and recovery of valuable products can be found in:

- electrocoat paint recovery
- oily waste water treatment
- textile industry (synthetic sizing agents and dyes)
- pulp and paper industry (printing ink recovery)
- leather and tanning industry effluents treatment

Applications in the food industry can be found in:

- dairy industry (fabrication of cheese and recovery of proteins from whey)
- sugar refining
- concentration of fruit juices, clarification of beverages
- vegetable protein processing
- egg white concentration
Biotechnological applications are:

- enzymes and micro-organisms separation and harvesting
- bioreactor processes and tissue culture systems

Application in Polymer industry:

- concentration of latex emulsions

Preparation of ultra-pure water (biotechnology, pharmaceutical and electronics industry) Hemofiltration (separation of microsolute from blood) Polymer industry: concentration of latex emulsions. The most recent economical evaluation of the membrane industry has been given by Strathmann (1992). At that moment, the most important UF application was hemofiltration, is the filtration of blood, to remove toxic metabolisms from the blood stream, such as urea, but retaining proteins and blood cells. The growth of the total membrane industry was estimated at 12-15% per year. The sales of the membrane industry in total (all types of membranes and modules) and of ultrafiltration membranes and modules in particular.

1.12.2 Applications of ultrafiltration in non-aqueous systems

The industrial, environmental, and medical ultrafiltration applications that were summarized above are almost without exception applications for aqueous mixtures. However, there is an enormous potential field for the application of ultrafiltration in non-aqueous systems, provided that there are commercially available membranes and modules that are suitable for applications involving organic solvents. The possible applications are solvent recovery and reuse in the petrochemical, painting, and polymer manufacturing industry, as well as upgrading of several product streams. There are only a few examples for applications of ultrafiltration in non-
aqueous solutions described in literature. Most of these descriptions can be found in the patent literature, and it often concerns separations of systems, which are very difficult or even impossible to separate by conventional separation techniques. In this section, some examples will be discussed in more detail.

1.12.3 Paint solvent recovery

During paint manufacturing and in automated painting baths, it is necessary to frequently change the type and colour of the paint. For this purpose, the just applied paint has to be removed from the mixing vessels and filling lines by means of rinsing with paint solvents. The solvents, contaminated with resins and pigments, are usually disposed of by incineration studied by Smallwood (1993). When applying an ultrafiltration process, paint solvents can be recovered from the waste stream, and can be reused for rinsing or as fresh paint solvents. The membranes used in this case are solvent resistant polyimide membranes reported by Iwama (1982) and Isooka (1984). The paint solvents were mixtures of approximately 60% aromatic hydrocarbons (toluene, xylene), 30% methyl ethyl ketone, and 10% of other ingredients (alcohols, esters).

1.12.4 Recovery of dewaxing aids during oil dewaxing processes

Crude waxy hydrocarbon oils are usually dewaxed by using mixtures of aliphatic ketones (acetone, methyl ethyl ketone), aromatic hydrocarbons (toluene, xylene) and halogenated hydrocarbons (chloroform, dichloroethane). In the patent literature there are a number of examples for the application of reverse osmosis to recover solvent from the dewaxed oil studied and reported by Wernick et al (1987), Hafez et al (1985) and Bitter et al (1988). The dewaxing aids, i.e., polyalkylacrylates, polyethyleneoxides, polyvinyl pyrrolidone, etc., remain in the solvent-free wax, recovery of these
components by conventional separation techniques is very difficult and costly. However, the dewaxing aids can be recovered by ultrafiltration of the wax at 70-100°C through a polyethersulfone or a polyimide membrane, while the purified wax can be used for other purposes. Ultrafiltration can also be employed in the dewaxing process itself. During the Exxon-DILCHILL process, the waxy oil is heated to just above its cloud point. Cold dewaxing solvent is added in small amounts to this mixture, so that small crystallites are formed. These crystallites can be removed by ultrafiltration separation this was reported by Lafreniere (1989).

1.12.5 Heavy oil upgrading or deasphalting

A vacuum distillation step is one of the typical processes during crude oil refinery. Products from this step are the so-called middle boiling distillates and heavy vacuum residual oil (HVR). The HVR is unsuitable for conventional cracking methods, since it contains several sulfur and metal containing compounds as well as polar components, that foul and deactivate the cracker catalysts. The general deasphalting step is performed in a flasher-stripper combination is studied by Gerhartz (1988) however, upgrading can be done more energy-efficiently by ultrafiltration of a mixture of HVR with toluene, chloroform, hexane or heptanes through various ultrafiltration membranes.

1.12.6 Treatment of used lubricating oil

Used lubricating oil contains several degraded components such as polymers, dispersion agents, and anti oxidants, as well as contaminants like asphaltenes, lead, and combustion by-products. After removal of these degraded components and contaminants, the regenerated oil can be reused as fuel. Ultrafiltration of a mixture of the used oil with solvent (hexane) through
polyacrylonitrile membranes showed very promising results, and most of the contaminants were removed from the oil.

1.12.7 Edible oil processing

In the edible oil industry, oil is extracted from its raw material (e.g., oilseeds, fruit pulps, animal remains or fish), with solvents such as hexane, ethanol, or isopropanol. After extraction, the mixture of 70-75% solvent with extracted oil (the miscella) is usually separated by distillation; however, an ultrafiltration or reverse osmosis process is also very effective and much more energy efficient. This has been reported by Köseoglu et al. (1990) and tested various “tight” commercial ultrafiltration and reverse osmosis membranes for this separation. They found that only one of these membranes was resistant enough to the miscella and was able to retain the oil (a reverse osmosis membrane with a MWCO of 300-400). In a Japanese patent this separation has been described using Nitto polyimide ultrafiltration membranes; this study was reported by Rinorui Oil Mills Co. and Nitto Electric Industrial Co. (1982).

1.12.8 Applications of ultrafiltration in the polymer processing industry

Some applications of non-aqueous ultrafiltration in the polymer industry have been described in Japanese patents. After manufacturing of diallylphthalate polymers in xylene (Tanaka et al. 1985), or polyolefins in hexane (Chisso 1983), or thermosetting resins in a toluene/xylene/DMF-mixture (Nitto Electric Industrial Co. 1981), the unreacted monomers and low molecular weight products can be removed by ultrafiltration; for all three processes, Nitto polyimide membrane modules have been used. Another application of ultrafiltration is the treatment of contaminated rinsing streams after washing of plastic molding or metal parts, using solvents such as
trichloroethylene. The contaminated solvent can be cleaned by a hybrid process of settling and ultrafiltration has been studied by Aikawa (1986) for this purpose, polysulfone membranes have been used.

1.13 SCOPE AND OBJECTIVES OF PRESENT INVESTIGATION

From the survey of literature, it is evident that the cellulose acetate (CA) based membranes offer many advantages over other membrane materials and also the hydrophilicity of the CA membrane can be improved by blending with the hydrophilic blend materials, but for all membranes they are highly fouling in nature. To reduce the fouling behaviour there is very few study has been reported. Though several reports on the properties and performance of various membranes are available, membranes suitable for specific environment and applications with improved properties such as flux, hydraulic resistance, rejection, mechanical, thermal and chemical stability of CA/(PVA/gelatin) have not been reported. Hence, in the present investigation, an attempt has been made to develop CA/(PVA/gelatin) UF membranes with improved properties for desired application. In this present study, cellulose acetate (CA) have been chosen as the base polymer and Polyvinyl alcohol(PVA)/gelatin pair has been chosen as blending polymer to find its influence on UF membrane performance.

In order to prepare ultrafiltration membranes with improved properties for protein separation with less fouling, an investigation on preparation of hydrophilic polymer blend membranes and their separation studies with the following objectives.

The main objective and scope of the present investigation are,
- Modification of cellulose acetate with bio material of PVA/gelatin pair to improve ultrafiltration properties.

- To study the effect of the composition of the PVA/gelatin pair on the performance of base cellulose acetate membrane.

- To characterize the modified membranes in terms of pure water flux, mechanical properties, morphology, protein rejection studies, molecular weight cut off and pore statistics.

- To study the fouling behavior of selected modified membranes.

- To fit a suitable mathematical model to study the permeate flux, membrane resistance and pore blocking on the surface of the membrane.

- To study the influence of concentration of PVA/gelatin pair on the ultrafiltration separation performance of membranes by using proteins such as Bovine Serum Albumin, Egg Albumin, Pepsin and Trypsin.